Application of a inhomogeneous sample model in the piezoelectric photothermal spectroscopy of mixed crystals.

M.Malinski [1] J.Zakrzewski [2]

1) Department of Electronics, Technical University of Koszalin
17 Partyzantow St, 75-411 Koszalin Poland

2) Institute of Physics Nicolaus Copernicus University
5/7 Grudziązka St, 87-100 Toruń Poland

Abstract

This paper presents the basic concepts of the inhomogeneous sample model. This is one of the models describing the piezoelectric photothermal (PPT) spectra observed for the mixed crystals. The PPT spectra both experimental and theoretical presented in this paper revealed the inhomogeneous character of the crystal structure in the case of AII-BVI mixed crystals. The analysis of the spectra enabled determination of both the basic optical parameters of two crystal regions, observed in the investigated samples, and their percentage composition.

1.Introduction

The piezoelectric photothermal spectroscopy (PPT) has recently become a practical method of the thermal and optical characterization of semiconductor materials. Recent advances in this field showed that this method enables determination of both optical and thermal parameters of semiconductor samples. It revealed however the necessity of development of a series of physical models of real samples. The analysis showed that the conclusions drawn from experimental piezoelectric amplitude and phase spectra depend in the essential way on the choice of the physical model of a sample. It turned out that one of the multi-layer models of the sample i.e. a inhomogeneous sample model is one of the most important models in the case of mixed crystals. In this paper the inhomogeneous sample model is described in detail and the results of computations performed in this model compared with the results of computations performed in a single layer model typical for the Jackson & Amer approach. The results presented in this paper comprise among others the computations of the amplitude PPT spectra of different inhomogeneous AII-BVI samples at different frequencies of modulation in the range from 3 Hz to 126 Hz. For simplicity the model in the two crystal regions approach is presented. All the computed spectra are compared with experimental spectra obtained for the same set of frequencies. The most spectacular are the results obtained among others for $Zn_{1-x}Be_xTe$ mixed crystals.

2. Sample preparation and experimental procedures.

Single crystals of AII-BVI semiconductors analyzed in this paper were grown from the melt by the high pressure Bridgman method under argon overpressure [1]. The crystals were cut into 0.1 cm thick plates , mechanically polished and chemically etched. Some samples were annealed in zinc vapour at the temperature 1230K for several hours. The piezoelectric photothermal (PPT) spectra were measured in the rear configuration with the PZT transducer attached to the back side of the sample. The signal was detected with the lock-in amplifier. All PPT spectra were measured at room temperature.

3. A inhomogeneous sample model.

In three component mixed crystals one can expect that the spatial distribution of ions in the crystal can be non-uniform. For example in the case of $Zn_{1-x}Be_xTe$ mixed crystals, exhibiting an average value x=0.07, a spatial distribution of Be is not uniform in the whole volume of the crystal. As a result different parts of the crystal exhibit different optical parameters. There are several multi-layer models describing different types of spatial distributions in the crystals: a single layer model, an inactive layer model, a inhomogeneous sample model, a depletion layer model , an enriched layer one or a model of superposition [2,3,4]. In this paper the model of a inhomogeneous sample is described in detail and illustrated with the experimental amplitude PPT spectra. In the model presented below the PPT spectra were computed in the two crystal region approach i.e. it is assumed that there are only two types of crystal regions exhibiting different optical parameters.

The schematic diagram of a crystal sample illustrating a inhomogeneous sample model is presented in Fig.1.

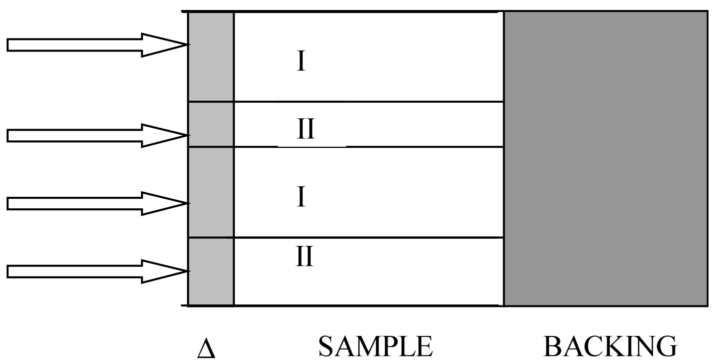


Fig1. Schematic diagram of a sample in a inhomogeneous sample model. I and II denote two crystal regions Δ is the thickness of a surface inactive layer, backing means in the case of investigated samples a steal hemisphere between the sample and a PZT transducer.

The spectra of the optical absorption coefficient of these regions I and II are determined by the set of basic parameters. The expressions describing the optical absorption coefficient spectra in the low and high absorption regions are given below

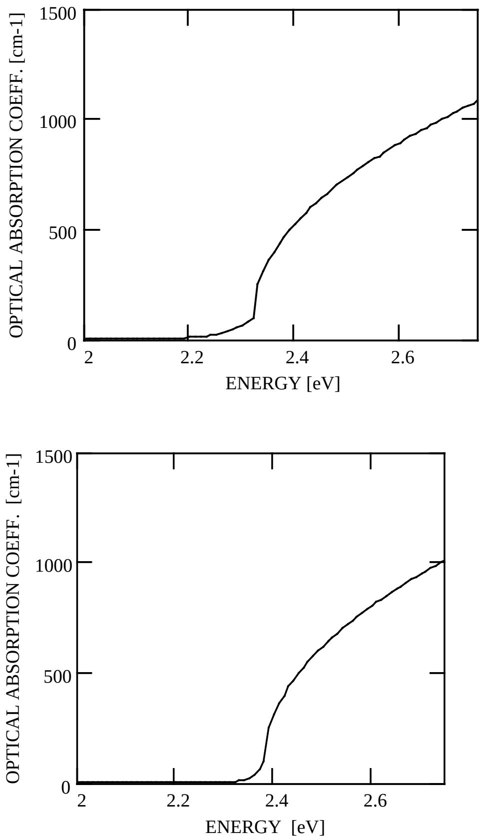
For $E_{exc} < E_g$
$$\beta(h\nu) = \beta_0 \cdot \exp\left((E_{exc} - E_g)\cdot \gamma / k \cdot T\right) \quad (1)$$

For $E_{exc} > E_g$
$$\beta(h\nu) = A_0 \cdot \sqrt{E_{exc} - E_g} + \beta_0 \quad (2)$$

The set of average values of these parameters obtained for $Zn_{1-x}Be_xTe$ mixed crystals when x=0.07 is given below.

E_{g1}=2.32 eV	E_{g2}=2.38 eV
β_{01}=100 cm^{-1}	β_{02}=80 cm^{-1}
γ_1=0.5	γ_2=1
A_{01}=1500 $cm^{-1}eV^{-1/2}$	A_{01}=1500 $cm^{-1}eV^{-1/2}$
α=0.2 cm^2/s	Δ=0.006 cm

The spectra of the optical absorption coefficient of these regions are presented in Fig.2.



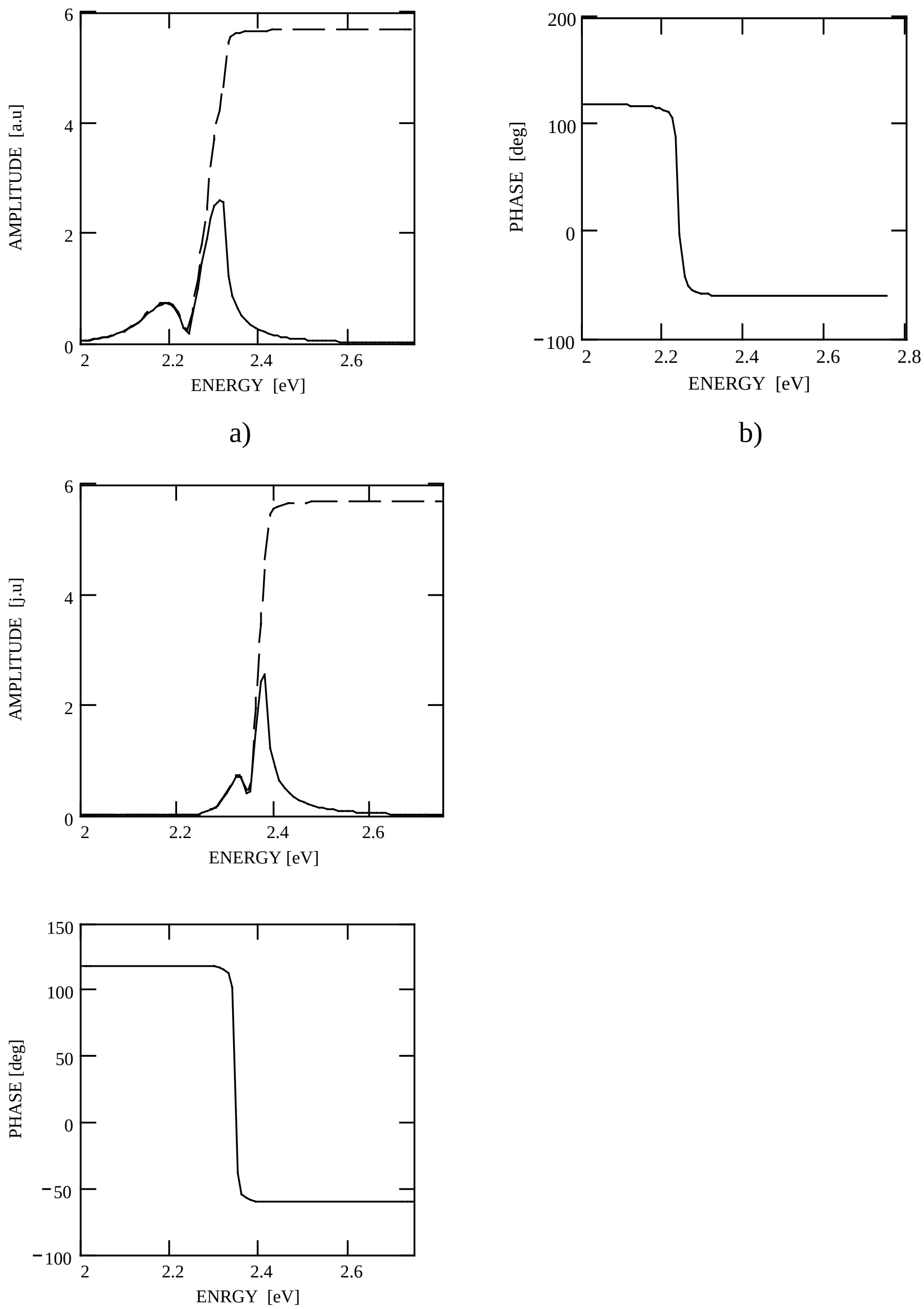
a) b)

Fig.2. Optical absorption coefficient spectra of the two crystal regions a) the first region exhibiting $E_{g1}=2.32\ eV$ and b) the second region of $E_{g2}=2.38\ eV$.

The PPT amplitude spectra computed for the above optical parameters and the thickness of the sample $l=0.1\ cm$, thermal diffusivity of the samples $\alpha=0.2\ cm^2/s$, thermal reflection coefficient between the sample and the backing $R=-1$ and the frequency of modulation $f=126Hz$ are presented in Fig.3. The computations of the PPT spectra for each of the crystal regions separately were performed, both in a modified single layer Jackson & Amer model [5] and in a depletion layer model, with a new temperature spatial distribution formulae $T(x)$ [6].

$$S \cong -C \cdot \left(\frac{1}{l} \cdot \int_0^l T(x) \cdot dx - \frac{6}{l^2} \cdot \int_0^l \left(\frac{l}{2} - x\right) \cdot T(x) \cdot dx\right)$$

(3)



c) d)

Fig.3. Amplitude and phase PPT spectra of the first (a,b) and the second (c,d) crystal region. Dash lines are the theoretical curves computed in a single layer model, solid lines are the theoretical curves computed in a model of an inactive layer with the thickness of a inactive layer Δ=0.006 cm.

The pictures above illustrate the influence of an inactive layer on the PPT amplitude spectra. An inactive layer decreases strongly the value of the amplitude of the signal for energies above the energy gap of the crystal in so called high absorption region. It does not influence at the same time the phase spectra. In a model of a inhomogeneous sample it is assumed that the piezoelectric signal that is measured is a superposition of the two piezoelectric signals S_1 and S_2 coming from the two crystal regions with the weighing factor *k*. The resulting piezoelectric signal is given by the equation (4).

$$S(h\nu)= S_1(h\nu)\cdot(1-k) + S_2(h\nu)\cdot k \tag{4}$$

The $Zn_{1-x}Be_xTe$ mixed crystals exhibited the PPT spectra that indicated the possibility of the complex crystal structure of the samples [7-10]. These spectra were next the subject of the modeling in the inhomogeneous sample model. Figures presented below show the experimental and theoretical amplitude PPT spectra of $Zn_{0.93}Be_{0.07}Te$ mixed crystals for different frequencies of modulations .

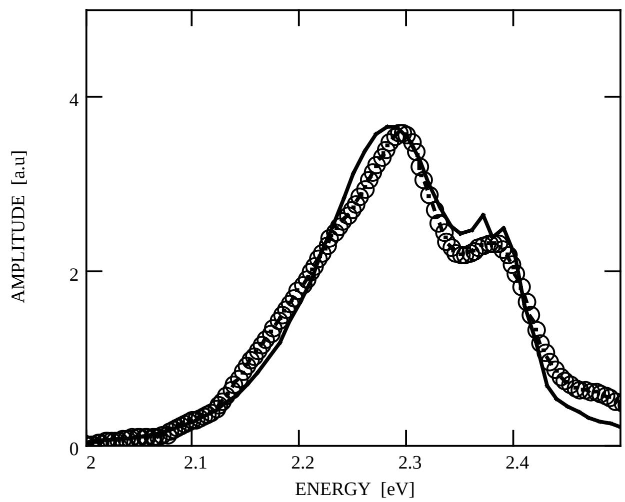


Fig.4. Amplitude PPT spectra for *3 Hz*. $E_{g1}=2.37$ *eV* $E_{g2}=2.42$ *eV* $k=0.42$. Circles – experimental results , solid line theoretical curve.

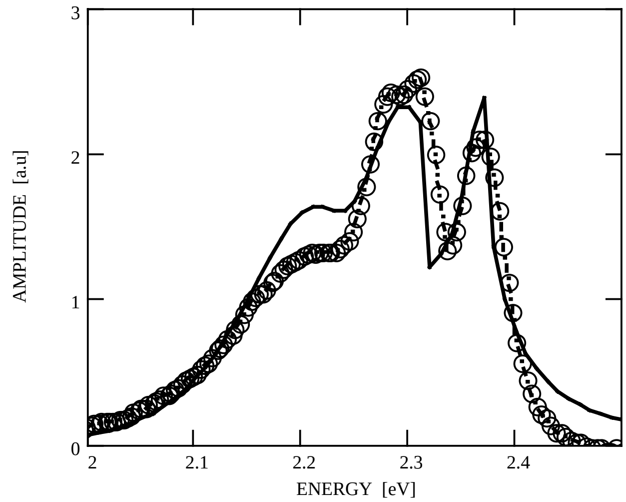


Fig.5. Amplitude PPT spectra for *16 Hz Eg1=2.31 eV, Eg2=2.37 eV k=0.42*. Circles- experimental results, solid line- theoretical curve.

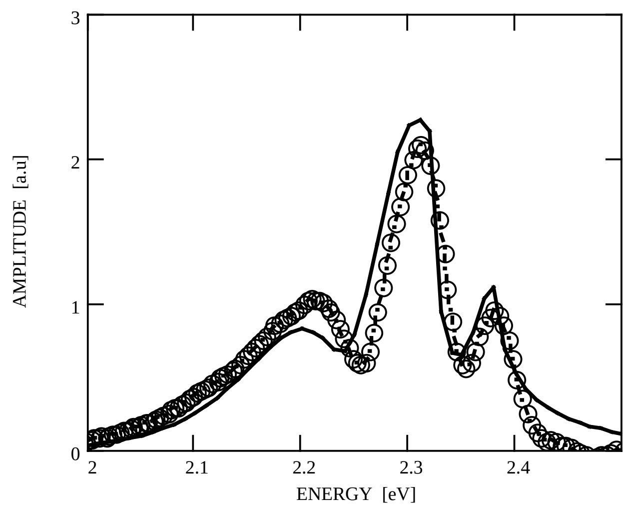


Fig.6. Amplitude PPT spectra for *36 Hz Eg1=2.32 eV, Eg2=2.38 eV k=0.25*. Circles- experimental results, solid line- theoretical curve.

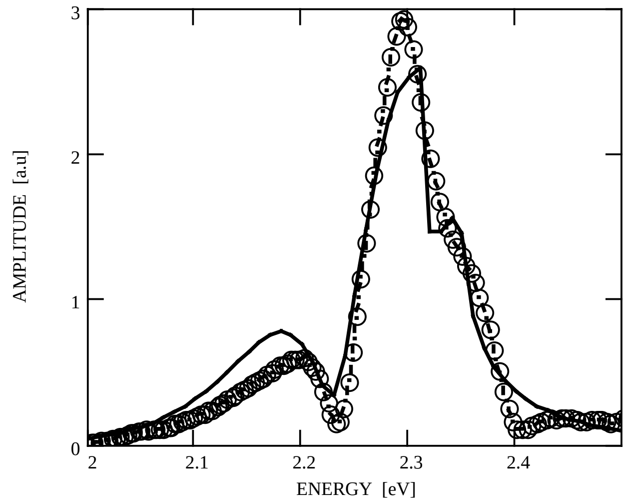


Fig.7. Amplitude PPT spectra for *76 Hz Eg1=2.31 eV, Eg2=2.35 eV k=0.25*. Circles- experimental results, solid line- theoretical curve.

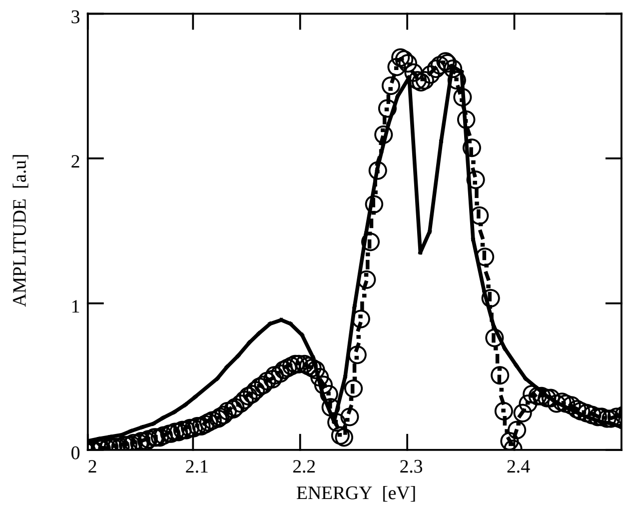


Fig.8. Amplitude PPT spectra for *126 Hz Eg1=2.30 eV, Eg2=2.35 eV k=0.4.* Circles- experimental results, solid line- theoretical curve.

The change of the PPT spectra is the result of the reflections of the thermal waves ,originally generated in the sample, from the backing material. For the samples analyzed above exhibiting thermal diffusivity $\alpha=0.2\ cm^2/s$, the thickness $l=0.1\ cm$ and low frequencies of modulation they were thermally thin. The influence of the reflections from the backing on the temperature distribution in the sample and as a consequence on the spectrum of the piezoelectric signal is stronger for the low absorption region than in the case of the high absorption one. That is why the low absorption part of the PPT spectra is modified stronger with the frequency of modulation than the high absorption one. If this explanation is correct then the change of the PPT spectra with the frequency of modulation should not be observed for the thermally thick samples where the contribution of the effect of reflection of thermal waves from the backing is negligible.

These expectations agree with the results of measurements performed for $Cd_{1-x}Mn_xTe$ mixed crystals [11]. The PPT spectrum of the $Cd_{0.51}Mn_{0.49}Te$ mixed crystal is presented in Fig.9. This spectrum exhibited two crystal regions with two different energy gaps $E_{g1}=2.035$ *eV* and $E_{g2}=2.105$ *eV* and two different thickness of inactive layer $\Delta_1=0.005$ *cm and* $\Delta_2=0$ *cm*. These crystals are more thermally insulating than $Zn_{1-x}Be_xTe$ crystals as they show thermal diffusivity in the range $\alpha=0.005\text{-}0.1\ cm^2/s$. Measurements of the PPT spectra of the $Cd_{0.51}Mn_{0.49}Te$ mixed crystal, for the frequencies of modulation *f=6, 36 and 126 Hz* , showed that all the spectra were identical with the one presented in Fig.9 measured for 76 Hz.

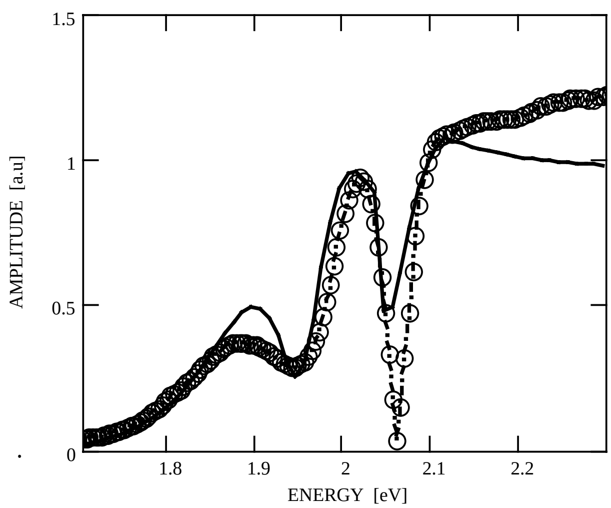


Fig.9. Amplitude PPT spectra of $Cd_{0.51}Mn_{0.49}Te$ mixed crystal for f=76 *Hz*, $l=0.1$ *cm*. Fitting parameters: : $E_{g1}=2.035$ *eV*, $\beta_{01}=130\ cm^{-1}$, $\gamma_1=0.5$, $A_{01}=1500$,$E_{g2}=2.105$ *eV*, $\beta_{02}=150\ cm^{-1}$, $\gamma_2=0.9$, $A_{02}=1500$, $\alpha=0.1\ cm^2/s$, $\Delta_1=0.005$ *cm*, $\Delta_2=0$ *cm*. *R=1, k=0.3.* Circles-experimental results, solid line- theoretical curve.

The computations performed in a model of inhomogeneous sample gave the same spectra for all these frequencies of modulation. No visible change of the shape of the PPT spectra was observed with the change of the frequency of modulation. This fact confirms the reason of the observed changes of the PPT spectra of thermally thin mixed crystals.

4.Conclusions

The general conclusion that was drawn from the results of computations performed in the inhomogeneous sample model was the following. It enables the determination of the percentage composition of the crystals described by ‘k’ parameter. It is possible to control the uniformity of the spatial distribution of components in the crystal. This model enables also the quantitative description of the quality of the surface by the parameter Δ being the thickness of an inactive layer. By the fitting procedure of the theoretical amplitude PPT spectra to the experimental ones it is possible to determine the set of basic optical parameters of the crystal regions. The physical reason of the observed changes of the PPT spectra was proposed. It is based on the model of reflections of thermal waves generated in the sample from the backing material.

References

1.F.Firszt, H.Męczyńska, B.Sekulska, J.Szatkowski, W.Paszkowicz, J.Kachniarz Semicond. Sci. Technol. 10, 197, (1995)

2..M.Maliński, J.Zakrzewski, H.Męczyńska Proc. 28th Int. Conf. German Acoustic Society March 2002 , Bohum Germany, 430

3..M.Maliński Mol. & Quantum Acoustics 23, 277, (2002)

4. M.Maliński, J.Zakrzewski Rev. Sci. Instr. 74(1), 598, (2003)

5.W.Jackson, N.M.Amer Appl. Phys. 51(6), 3343, (1980)

6.M.Maliński Archives of Acoustics 27(3), 217, (2002)

7. J.Zakrzewski Ph Doctor Thesis UMK Toruń 2001

8.J.Zakrzewski, F.Firszt, S.łęgowski, H.Męczyńska, A.Marasek Proc.28th Int.Conf.DAGA March 2002, Bochum Germany, 438, (2002)

9.W.Paszkowicz, F.Firszt, S.Łęgowski, H.Męczyńska ,J.Zakrzewski, M.Marczak Phys.Stat.Sol.(b) 229(1),57, (2002)

10. F.Firszt, S.Łęgowski, H.Męczyńska, J.Szatkowski, J.Zakrzewski Anal.Sciences 17, 129, (2001)

11. J.Zakrzewski, F.Firszt, S.Łęgowski, H.Męczyńska, A.Marasek, M.Pawlak Rev.Sci. Instr. 74(1), 573,(2003)